

PATENT  
0649-0789P

IN THE U.S. PATENT AND TRADEMARK OFFICE

APPLICANT: Yasuhiro YOSHIOKA                      CONF. NO.: 3458  
SERIAL NO:    09/899,261                      GROUP:    1752  
FILED:            July 6, 2001                      EXAMINER: Thorl Chea  
FOR:              PHOTOTHERMOGRAPHIC MATERIAL

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Yasuhiro YOSHIOKA, declare the following.

I graduated from the University of Tokyo, Faculty of Science with a Master's Degree in Course of Chemistry in March of 1980.

I have been employed by Fuji Photo Film Co. Ltd. (Fuji), since April of 1980.

I have been engaged in research regarding new couplers at Ashigara Research Laboratories at Fuji from 1980 to 1998.

I have been engaged in research regarding photothermographic materials at Ashigara Research Laboratories at Fuji since 1999.

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I am the inventor of the disclosure of the above-captioned application. I am fully knowledgeable of the disclosure of the application and field of art of the present invention.

The following experiments were conducted by me or under my direct supervision.

General Discussion

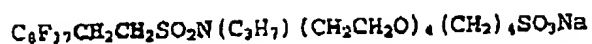
The experimental evidence described in the present specification is reiterated herein for the Examiner's convenience. In addition, four new experiments not previously disclosed are presented. In all of these experiments, the unexpectedly superior resistance to white spots of the inventive photothermographic material incorporating a surface active agent of formula (F) wherein  $n=1$  is shown.

In the four new experiments, a comparison was made between the instantly claimed photothermographic material containing a surface active agent compound FS-13 and essentially the same photothermographic material except that the surface active agent has been replaced with the compound FC-4 disclosed by Toya (U.S. Patent 5,698,380) at column 17, line 38.

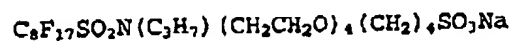
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The structure of the compounds are as follows:

FS-13 -



FC-4 -



As can be seen from these structures, FS-13 is a surface active agent of formula (F) wherein  $n = 1$  whereas FC-4 is a surface active agent of formula (F) wherein  $n = 0$ . Since the presently amended claims recite that  $n = 1$ , the compound FC-4 which lacks a " $\text{CH}_2\text{CH}_2$ " near the fluorinated end falls outside the scope of the present invention.

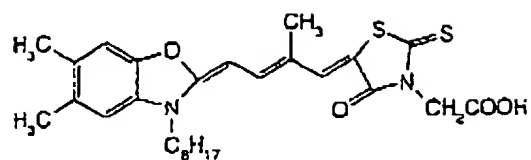
#### Experimental Protocol And Results

##### EXAMPLE 1

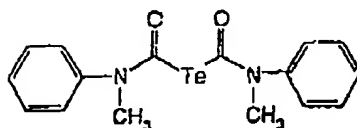
The structures of the compounds used in the examples are shown below.

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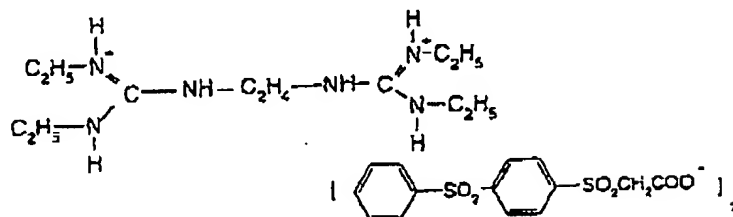
## Spectral sensitizing dye A



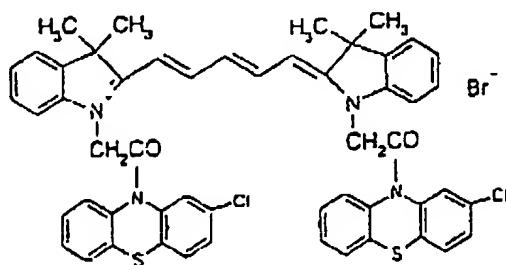
## Tellurium sensitizing dye B



## Base precursor compound 11

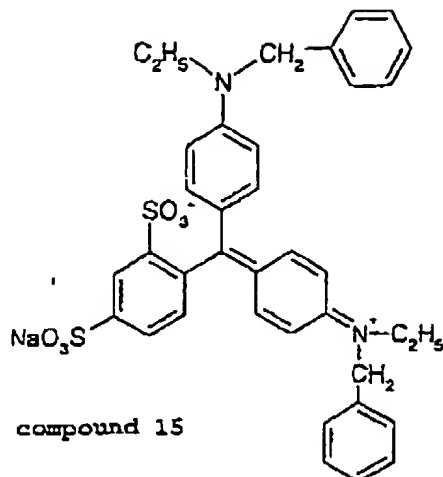


## Cyanine dye compound 13

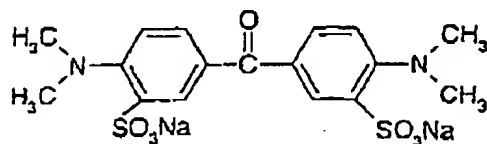


Blue dye compound 14

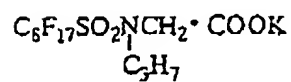
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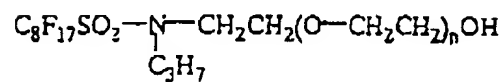
Yellow dye compound 15



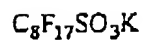
FC-1



FC-2

 $n \approx 14.9$ 

FC-3



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(Preparation of PET support)

Using terephthalic acid and ethylene glycol, according to an ordinary method, PET having a specific viscosity  $IV = 0.66$  (measured in phenol/tetrachloroethane = 6/4 (weight ratio) at 25°C) was obtained. After forming pellets from the polymer, the pellets were dried at 130°C for 4 hours, after melting at 300°C, the molten pellets were extruded from a T-type die and quickly cooled to prepare an unstretched film having a thickness that the film thickness after thermal fixing became 175  $\mu m$ . The film was stretched to the lengthwise direction 3.3 times using rolls each having a different peripheral speed and then stretched to the width direction 4.5 times by a tenter. In this case, the temperatures were 110°C and 130°C respectively. Thereafter, after thermally fixing at 240°C for 20 seconds, the film was relaxed 4% to the width direction at the same temperature. Then, after slitting the chuck portion of the tenter, knurl work was applied to both ends, the film was wound at 4  $kg/cm^2$  to obtain a roll of the film having a thickness of 175  $\mu m$ .

(Surface corona treatment)

Using a solid state corona treating machine, Model 6 KVA, manufactured by Pillar Co., both surfaces of the support were treated at room temperature at 20 meters/minute. In this case, from the values of the electric current and the electric voltage, it was confirmed that the treatment of 0.375

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kV·A·minute/m<sup>2</sup> was applied to the support. In this case, the treatment frequency was 9.6 kHz and the gap clearance between the electrode and the dielectric roll was 1.6 mm.

(Preparation of subbed support)

(1) Preparation of coating solution of subbing layer

Formula (1) (for subbing layer of the light-sensitive layer side)

Pesresin A-515CB (30 wt.% solution) manufactured by Takamtsu Yusbi K.K.	234 g
Polyethylene glycol monononyl phenyl ether (mean ethylene oxide No. = 8.5) 10 wt.% soln.	21.9 g
MP-1000 (polymer fine particles, mean particle size 0.4 µm, made by Soken Kagaku K.K.)	0.91 g
Distilled water	744 ml

Formula (2) (for the 1st back layer)

Styrene-butadiene copolymer latex (solid components 40 wt.%, styrene/butadiene wt. ratio = 68/32)	158 g
2,4-Dichloro-6-hydroxy-S-triazine sodium salt 8 wt.% aqueous solution	20 g
Sodium laurylbenzenesulfonate 1 wt.% aq. soln.	10 ml
Distilled water	854 ml

Formula (3) (for 2nd layer of back layer side)

SnO <sub>2</sub> /SbO (9/1 wt. ratio, mean particle size 0.038 µm, 17 wt.% dispersion)	84 g
Gelatin (10 wt.% aqueous solution)	89.2 g

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Metrose TC-5 (2 wt.% aqueous solution)

made by Shin-Etsu Chemical Co., Ltd.) 8.6 g

MP-1000, made by Soken Kagaku K.K. 0.01 g

Sodium dodecylbenzenesulfonate 1 wt.% aq. soln.

10 ml

NaOH (1 wt.%) 6 ml

Proxel (made of I. C. I. Co.) 1 ml

Distilled water 805 ml

(Preparation of subbed support)

After applying the above-described corona discharging treatment to both surfaces of the above-described biaxially stretched polyethylene terephthalate support having the thickness of 175  $\mu\text{m}$ , the above-described formula (1) of the subbing coating solution was coated on one surface thereof by a wire bar such that the wet coated amount became 6.6  $\text{ml}/\text{m}^2$  (per one surface) and dried at 180°C for 5 minutes. Then, the above-described formula (2) for the subbing coating solution was coated on the back surface by a wire bar such that the wet coating amount became 5.7  $\text{ml}/\text{m}^2$  followed by drying at 180°C for 5 minutes, and further the above-described formula (3) for the subbing coating solution was coated on the back surface by a wire bar such that the wet coated amount became 7.7  $\text{ml}/\text{m}^2$  followed by drying at 180°C for 6 minutes to prepare a subbed support.

(Preparation of coating solution of back surface)



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(Preparation of solid fine particle dispersion (a) of base precursor)

A mixture of 64 g of the base precursor compound 11, 28 g of diphenylsulfone, 10 g of a surface active agent, Demor N manufactured by Kao Corporation, and 220 ml of distilled water was beads dispersed using a sand mill (1/4 Gallon Sand Grinder Mill, manufactured by AIMEX Corporation) to obtain the solid fine particle dispersion (a) of the base precursor compound having a mean particle size of 0.2  $\mu\text{m}$ .

(Preparation of dye solid fine particle dispersion)

A mixture of 9.6 g of the cyanine dye compound 13, 5.8 g of sodium p-dodecylbenzenesulfonate, and 305 ml of distilled water was beads dispersed using a sand mild (1/4 Gallon Sand Grinder Mill, manufactured by AIMEX Corporation) to obtain a dye solid fine particle dispersion having a mean particle size of 0.2  $\mu\text{m}$ .

(Preparation of coating solution of antihalation layer)

By mixing 17 g of gelatin, 9.6 g of polyacrylamide, 70 g of the above-described solid fine particle dispersion (a) of the base precursor, 56 g of the above-described dye solid fine particle dispersion, 1.5 g of polymethyl methacrylate fine particles (mean particle size 6.5  $\mu\text{m}$ ), 0.03 g of benzoisothiazolinone, 2.2 g of sodium polyethylenesulfonate, 0.2 g of the blue dye compound 14, 3.9 g of the yellow dye compound 15, and 844 ml of water, the coating solution of an antihalation layer was prepared.

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(Preparation of coating solution of protective layer for back surface)

In a vessel maintained at 40°C, by mixing 50 g of gelatin, 0.2 g of sodium polystyrenesulfonate, 2.4 g of N,N-ethylenebis(vinylsulfonacetamide), 1 g of sodium t-octylphenoxyethanesulfonate, 30 ml of benzoisothiazolinone, 37 mg of N-perfluorooctylsulfonyl-N-propylalanine potassium salt, 0.15 g of polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether (ethylene oxide average polymerization degree 15), 32 mg of  $C_8F_{17}SO_3K$ , 64 mg of  $C_8F_{17}SO_2(C_2H_5)(CH_2CH_2O)_4(CH_2)_4-SO_3Na$ , 8.8 g of an acrylic acid/ethyl acrylate copolymer (copolymerization weight ratio 5/95), 0.6 g of Aerosol OT (manufactured by American Cyanamid Company), 1.8 g of a fluid paraffin emulsion as fluid paraffin, and 950 ml of water, a coating solution of a protective layer for the back surface was prepared.

(Preparation of silver halide emulsion 1)

To 1421 ml of distilled water was added 3.1 ml of a solution of 1% by weight potassium bromide, and further 3.5 ml of sulfuric acid of 0.5 mol/liter in concentration and 31.7 g of phthalated gelatin were added thereto. The solution obtained was stirred in a stainless steel-made reaction jar at a solution temperature of 34°C, and the total amounts of a solution A obtained by adding distilled water to 22.22 g of silver nitrate to dilute to 95.4 ml and a solution B obtained by adding

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distilled water to 15.9 g of potassium bromide to dilute to 97.4 ml were added at a definite flow rate over a period of 45 seconds. Thereafter, 10 ml of an aqueous solution of 3.5% by weight hydrogen peroxide was added to the mixture and further 10.8 ml of 10% by weight benzimidazole was added thereto. Furthermore, the whole amount of a solution C obtained by adding distilled water to 51.86 g of silver nitrate to dilute to 317.7 ml was added thereto at a definite flow rate over a 20 minutes period and a solution D obtained by adding distilled water to 45.8 g of potassium bromide to dilute to 400 ml was added thereto by a controlled double jet method while keeping the pAg at 8.1. The whole amount of potassium hexachloroiridate(III) was added 10 minutes after the initiation of the additions of the solution C and the solution D such that the content thereof became  $1 \times 10^{-4}$  mol per mol of silver. Also, the whole amount of an aqueous solution of potassium iron(II) hexacyanide was added 5 seconds after the finish of the addition of the solution C such that the content became  $3 \times 10^{-4}$  mol per mol of silver. The pH of the mixture was adjusted to 3.8 using sulfuric acid having a concentration of 0.5 mol/liter, stirring was stopped, and then precipitation/desalting/water washing steps were carried out. Then the pH was adjusted to 5.9 using an aqueous solution of sodium hydroxide having a concentration of 1 mol/liter to prepare a silver halide dispersion having the pAg of 8.0.

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The above-described silver halide dispersion was kept at 38°C with stirring, 5 ml of a methanol solution of 0.34% by weight 1,2-benzisothiazolin-3-one was added, after 40 minutes, a methanol solution of the spectral sensitizing dye A was added in an amount of  $1 \times 10^{-3}$  mol per mol of silver, and after one minute, the temperature was raised to 47°C. Twenty minutes after the temperature raising, a methanol solution of sodium benzenethiosulfonate was added at  $7.6 \times 10^{-5}$  mol per mol of silver, and further after 5 minute since then, a methanol solution of the tellurium sensitizer B was added at  $1.9 \times 10^{-4}$  mol per mol of silver followed by carrying out ripening for 91 minutes. Then, 1.3 ml of a methanol solution of 0.8% by weight N,N'-dihydroxy-N"-diethylmelamine was added, and after 4 minutes since then, a methanol solution of 5-methyl-2-mercaptobenzimidazole was added at  $3.7 \times 10^{-3}$  mol per mol of silver and also a methanol solution of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole was added at  $4.9 \times 10^{-3}$  mol per mol of silver to prepare a silver halide emulsion 1.

The silver halide grains in the silver halide emulsion prepared were pure silver bromide grains having a mean equivalent sphere diameter of 0.046  $\mu\text{m}$  and the variation coefficient of the equivalent sphere diameters of 20%. The grain sizes, etc., were obtained from the average of 1000 grains using an electron microscope. The {100} face ratio of the grains was determined to be 80% using a Kubelka-Munk method.

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(Preparation of silver halide emulsion 2)

By following the same procedure as the preparation of the silver halide emulsion 1 except that the solution temperature 34°C at the grain formation was changed to 49°C, the addition time of the solution C was changed to 30 minutes, and potassium iron(II) hexacyanide was not added, a silver halide emulsion 2 was prepared. As the case of the silver halide emulsion 1, precipitation/desalting/water washing/dispersion steps were carried out. Furthermore, as the case of the emulsion 1 except that the addition amount of the spectral sensitization dye A was changed to  $7.5 \times 10^{-4}$  mol per mol of silver, the addition amount of the tellurium sensitizer B was changed to  $1.1 \times 10^{-4}$  mol per mol of silver, and the addition amount of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole was changed to  $3.3 \times 10^{-3}$  mol to mol of silver, the spectral sensitization, the chemical sensitization, and the addition of 5-methyl-2-mercaptobenzimidazole and 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole were carried out to obtain the silver halide emulsion 2. The emulsion grains of the silver halide emulsion 2 were pure silver bromide cubic grains having a mean equivalent sphere diameter of 0.080  $\mu\text{m}$  and the variation coefficient of equivalent sphere diameters of 20%.

(Preparation of silver halide emulsion 3)

By following the same procedure as the preparation of the silver halide emulsion 1 except that the solution temperature 34°C at the grain formation was changed to 27°C, a silver halide

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emulsion 3 was prepared. Also, as the case of the silver halide emulsion 1, precipitation/desalting/water washing/dispersion steps were carried out. By the same manner as the case of the emulsion 1 except that the addition amount of the spectral sensitizing A was changed to  $6 \times 10^{-3}$  mol per mol of silver as the solid dispersion (aqueous gelatin solution), and the addition amount of the tellurium sensitizer B was changed to  $5.2 \times 10^{-4}$  mol per mol of silver, the silver halide emulsion 3 was obtained. The emulsion grains of the silver halide emulsion 3 were pure silver bromide cubic grains having a mean equivalent sphere diameter of 0.038  $\mu\text{m}$  and the variation coefficient of equivalent sphere diameters of 20%.

(Preparation of mixed emulsion A for coating solution)

After mixing 70% by weight the silver halide emulsion 1, 15% by weight the silver halide emulsion 2, and 15% by weight of the silver halide emulsion 3, an aqueous solution of 1% by weight of benzothiazolium iodide was added to the mixture at  $7 \times 10^{-3}$  mol per mol of silver to prepare the mixed emulsion A for coating solution.

(Preparation of fatty acid silver salt dispersion)

After mixing 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 liters of distilled water, 49.2 liters of an aqueous solution of 5 mol/liter of NaOH, and 120 liters of tert-butanol, the reaction was carried out with stirring at 75°C for one hour to obtain a solution of

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sodium behenate. Apart from this, 206.2 liters of an aqueous solution of 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C. A reaction vessel containing 635 liters of distilled water and 30 liters of tert-butanol was kept at 30°C, and the total amount of the above-described sodium behenate solution and the total amount of the aqueous silver nitrate solution were added with stirring at definite flow rates over periods of 62 minutes and 10 seconds and 60 minutes respectively. In this case, the additions of the solutions were carried out such that for 7 minutes and 20 seconds after initiating the addition of the aqueous silver nitrate solution, the aqueous silver nitrate solution only was added, and thereafter, the addition of the aqueous sodium behenate solution was initiated, and for 9 minutes and 30 seconds after finishing the addition of the aqueous silver nitrate solution, the sodium behenate solution only was added. In this case, the temperature in the reaction vessel was 30°C and the outer temperature was controlled so that the solution temperature became constant. Further, a pipe of an addition system of the sodium behenate solution was insulated with steam trace, and the opening of a valve for steam was controlled so that the solution temperature at an outlet of a tip of an addition nozzle became 75°C. Also, piping of the addition system of the aqueous silver nitrate solution was kept warm by circulating cold water through an outside of a double pipe. The adding position of the aqueous

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sodium behenate solution and the adding position of the aqueous silver nitrate were symmetrical disposition with the stirring axis at the center, and also the positions were controlled at the heights of not contacting with the reaction solution.

After finishing the addition of the sodium behenate solution, the mixture was allowed to stir at the temperature for 20 minutes and then the temperature was lowered to 25°C. Thereafter, solid component was collected by a suction filtration and was washed with water until the electric conductivity of the filtrate became 30  $\mu\text{S}/\text{cm}$ . Thus, the fatty acid silver salt was obtained. The solid component was stored as a wet cake without drying.

When the form of the silver behenate grains obtained were evaluated from an electron microphotograph, the grains were flaky crystals having  $a = 0.14 \mu\text{m}$ ,  $b = 0.4 \mu\text{m}$ , and  $c = 0.6 \mu\text{m}$  in mean values ( $a$ ,  $b$ , and  $c$  were defined above), an average aspect ratio of 5.2, an average equivalent sphere diameter of 0.52  $\mu\text{m}$ , and the variation coefficient of the equivalent sphere diameters of 15%.

To the wet cake corresponding to 100 g of dry solid component were added 7.4 g of polyvinyl alcohol (PVA-217, trade name) and water to make 385 g of the total amount and the mixture was pre-dispersed by a homo-mixer.

Then, the pre-dispersed solution was treated 3 times by a dispersing machine (Microfluidizer M-110S-EH, trade name,



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manufactured by Microfluidex International Corporation, the use of G10Z intraction chamber) by controlling the pressure to 1750 kg/cm<sup>2</sup> to obtain a silver behenate dispersion. The cooling operation was carried out by mounting each of a coiled heat exchanger to before and behind of an interaction chamber and controlling the temperature of the refrigerant, whereby the dispersing temperature was established to 18°C.

(Preparation of 25% by weight dispersion of reducing agent)

To 10 kg of 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane and 10 g of an aqueous solution of 20% by weight modified polyvinyl alcohol (Poval MP203, manufactured by KURARAY CO., LTD.) was added 16 kg of water followed by mixing well to form a slurry. The slurry was sent by a diaphragm pump and dispersed by a horizontal sand mill (UVM-2: AIMEX Corporation) packed with zirconia beads having a mean diameter of 0.5 mm for 3 hours and 30 minutes, and thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added to control such that the concentration of the reducing agent became 25% by weight to obtain a reducing agent dispersion. In the reducing agent particles contained in the reducing agent dispersion thus obtained, the median size was 0.42  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The reducing agent dispersion was filtered with a polypropylene-made filter having a pore size of 10.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc., and stored.

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(Preparation of 25% by weight dispersion of reducing agent complex)

To 10 kg of a 1 : 1 complex of 2,2-methylenebis(4-ethyl-6-tert-butylphenol) and triphenylenephosphine oxide and 10 kg of an aqueous solution of 20% by weight modified polyvinyl alcohol (Poval MP203, manufactured by KURARAY CO., LTD.) was added 16 kg of water and the mixture was stirred well to form a slurry. The slurry was sent by a diaphragm pump and dispersed by a horizontal sand mill (UVM-2: AIMEX Corporation) packed with zirconia beads having a mean diameter of 0.5 mm for 3 hours and 30 minutes, and thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added to control such that the concentration of the reducing agent became 25% by weight to obtain a reducing agent complex dispersion. In the reducing agent complex particles contained in the reducing agent complex dispersion thus obtained, the median size was 0.46  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The reducing agent complex dispersion obtained was filtered with a polypropylene-made filter having a pore size of 10.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc. and stored.

(Preparation of 10% by weight dispersion of mercapto compound)

To 5 kg of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole and 5 kg of an aqueous solution of 20% by weight modified polyvinyl alcohol (Poval MP203, manufactured by KURARAY CO., LTD.) was added 8.3 kg of water and the mixture was stirred well to form a

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slurry. The slurry was sent by a diaphragm pump and dispersed by a horizontal sand mill (UVM-2: AIMEX Corporation) packed with zirconia beads having a mean diameter of 0.5 mm for 6 hours, and thereafter, water was added such that the concentration of the mercapto compound became 10% by weight to obtain a mercapto compound dispersion. In the mercapto compounds particles contained in the mercapto compound dispersion thus obtained, the median size was 0.40  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The mercapto compound dispersion obtained was filtered with a polypropylene-made filter having a pore size of 10.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc. and stored. Also, the dispersion was again filtered with a polypropylene-made filter having a pore size of 10.0  $\mu\text{m}$  directly before use.

(Preparation of 20% by weight dispersion-1 of organic polyhalogen compound)

A mixture of 5 kg of tribromomethylnaphthylsulfone, 2.5 kg of an aqueous solution of 20% by weight modified polyvinyl alcohol (Poval MP203, manufactured by KURARAY CO., LTD.), 213 g of an aqueous solution of 20% by weight sodium triisopropylphthalenesulfonate, and 10 kg of water was mixed well to form a slurry. The slurry was sent by a diaphragm pump and dispersed by a horizontal sand mill (UVM-2: AIMEX Corporation) packed with zirconia beads having a mean diameter of 0.5 mm for 5 hours, and thereafter, 0.2 g of a

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benzothiazolinone sodium salt and water were added to the dispersion such that the concentration of the organic halogen compound became 20% by weight to obtain an organic polyhalogen compound dispersion. In the organic polyhalogen compound particles contained in the organic polyhalogen compound dispersion thus obtained, the median size was 0.36  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The organic polyhalogen compound dispersion obtained was filtered with a polypropylene-made filter having a pore size of 3.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc. and stored.

(Preparation of 25% by weight dispersion-2 of organic polyhalogen compound)

By following the same procedure as the case of the 20% by weight dispersion-1 of organic polyhalogen compound except that 5 kg of tribromomethyl(4-(2,4,6-trimethylphenylsulfonyl)phenyl)sulfone was used in place of 5 kg of tribromomethylnaphthylsulfone, an organic polyhalogen compound dispersion was obtained, and the organic polyhalogen compound dispersion was diluted such that the concentration of the compound became 25% by weight and filtered. In the organic polyhalogen compound particles contained in the organic polyhalogen compound dispersion thus obtained, the median size was 0.38  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The organic polyhalogen compound dispersion obtained was

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filtered with a polypropylene-made filter having a pore size of 3.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc. and stored.  
(Preparation of 26% by weight dispersion-3 of organic polyhalogen compound)

By following the same procedure as the case of preparing 20% by weight dispersion-1 of organic polyhalogen compound except that 5 kg of tribromomethylphenylsulfone was used in place of 5 kg of tribromomethylnaphthylsulfone, an organic polyhalogen compound dispersion was obtained, and the dispersion was diluted such that the concentration of the organic halogen compound became 26% by weight, and the diluted dispersion was filtered. In the organic polyhalogen compound particles contained in the organic polyhalogen compound dispersion thus obtained, the median size was 0.41  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The organic polyhalogen compound dispersion obtained was filtered with a polypropylene-made filter having a pore size of 3.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc. and stored. Also, after storing, the dispersion was stocked at a temperature of not higher than 10°C before use.

(Preparation of 25% by weight dispersion-4 of organic polyhalogen compound)

By following the same procedure as the case of preparing 20% by weight dispersion-1 of organic polyhalogen compound except that 5 kg of tribromomethyl-3-pentanoylaminophenylsulfone

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was used in place of 5 kg of tribromomethylnaphthylsulfone, an organic polyhalogen compound dispersion was obtained, and the dispersion was diluted such that the concentration of the organic halogen compound became 25% by weight, and the diluted dispersion was filtered. In the organic polyhalogen compound particles contained in the organic polyhalogen compound dispersion thus obtained, the median size was 0.41  $\mu\text{m}$  and the largest particle size was not larger than 2.0  $\mu\text{m}$ . The organic polyhalogen compound dispersion obtained was filtered with a polypropylene-made filter having a pore size of 3.0  $\mu\text{m}$  to remove foreign matters such as dusts, etc. and stored.

(Preparation of 5% by weight solution of phthalazine compound)

In 174.57 kg of water was dissolved 8 kg of modified polyvinyl alcohol MP203, manufactured by KURARAY CO., LTD., and then 3.15 kg of an aqueous solution of 20% by weight sodium triisopropylphthalenesulfonate and 14.28 kg of 6-isopropylphthalazine were added to the solution to prepare a solution of 5% by weight 6-isopropylphthalazine.

(Preparation of 20% by weight dispersion of pigment)

To 250 g of water were added 64 g of C.I. Pigment Blue 60 and 6.4 g of Demor N, manufactured by Kao Corporation, and the mixture was mixed well to form a slurry. Then, 800 g of zirconia beads having a mean diameter of 0.5 mm were placed in a vessel together with the slurry and the slurry was dispersed by a dispersing machine (1/4 G Sand Grinder Mill, manufactured by

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AIMEX Corporation) for 25 hours to obtain a pigment dispersion. The pigment particles contained in the pigment dispersion thus obtained had a mean particle size of 0.21  $\mu\text{m}$ .

(Preparation of 40% by weight SBR latex)

An ultra-filtration (UF) purified SBR latex was obtained as follows.

The SBR latex described below was diluted to 10 times with distilled water, purified using Module FS03-FC-FUY03A1 for UF-purification (manufactured by Daisen Membrane System K.K.) until the ionic conductivity became 1.5 mS/cm, and Sundet-BL (manufactured by SANYO CHEMICAL INDUSTRIES, LTD.) was added thereto at 0.22% by weight. Furthermore, NaOH and  $\text{NH}_4\text{OH}$  were added such that  $\text{Na}^+$  ion :  $\text{NH}_4^+$  ion = 1 : 2.3 (mol ratio) and the pH was adjusted to 8.4. In this case, the latex concentration was 40% by weight.

(SRB latex; Latex of -St(68)-Bu(29)-AA(3)-,  $T_g = 17^\circ\text{C}$ )

The mean particle size was 0.1  $\mu\text{m}$ , the concentration was 45% by weight, the equivalent moisture content at 25°C, 60% RH was 0.6% by weight, the ionic conductivity was 4.2 mS/cm (the ionic conductivity was measured using conductivity meter CM-30S, manufactured by Toa Denpa Kogyo K.K., about the latex dope (40% by weight) at 25°C), and pH was 8.2.

(Preparation of coating solution of emulsion layer (light-sensitive layer))

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To a mixture of 1.1 g of the 20% by weight dispersion of the pigment, 103 g of the fatty acid silver salt dispersion, 5 g of the 20% by weight aqueous solution of polyvinyl alcohol PVA-205 (manufactured by KURARAY CO., LTD.), 5 g of the 25% by weight dispersion of the reducing agent, 16.3 g of the total amounts of 5 : 1 : 3 (weight ratio) of the organic polyhalogen compound dispersions-1, -2, and -3, 6.2 g the 10% by weight dispersion of the mercapto compound, 106 g of 40% by weight the SBR latex (T<sub>g</sub>: 17°C) purified by ultrafiltration(UF) and pH adjusted, and 18 ml of the 5% by weight solution of the phthalazine compound, obtained as described above was added 10 g of the silver halide mixed emulsions A directly before coating followed by mixing well to form a coating solution of emulsion layer, the coating solution was sent as it was to a coating die such that the coating amount became 70 ml/m<sup>2</sup>, and was coated.

The viscosity of the coating solution of emulsion layer measured by a B-type viscometer manufactured by Tokyo Keiki K.K. was 85 (mPa·s) at 40°C (No. 1 rotor, 60 rpm).

Also, the viscosities of the coating solution at 25°C measured using an RFS Froude Spectrometer manufactured by Rheometrix Far East Co., in the shear rates of 0.1, 1, 10, 100, and 1000 (1/second) were 1500, 220, 70, 40, and 20 (mPa·s) respectively.

(Preparation of coating solution of emulsion surface interlayer)



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To 772 g of the 10% by weight aqueous solution of polyvinyl alcohol PVA-205 (manufactured by KURARAY CO., LTD.), 5.3 g of the 20% by weight dispersion of the pigment, and 226 g of the 27.5% by weight solution of the methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization weight ratio 64/9/20/5/2) latex were added 2 ml of the 5% by weight aqueous solution of 'Aerosol OT' (manufactured by American Cyanamid Company), 10.5 ml of the 20% by weight aqueous solution of di-ammonium phthalate, and water to make the total amount 880 g, and the pH of the mixture was adjusted to 7.5 with NaOH to prepare a coating solution of an interlayer, and the coating solution was sent to a coating die such that the coating amount became 10 ml/m<sup>2</sup>.

The viscosity of the coating solution measured by a B-type viscometer was 21 (mPa s) at 40°C (No. 1 rotor, 60 rpm).  
(Preparation of coating solution of 1st protective layer of emulsion layer surface)

In water was dissolved 64 g of inert gelatin, to the gelatin solution formed were added 80 g of the 27.5% by weight solution of the methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization weight ratio 64/9/20/5/2) latex, 23 ml of the 10% by weight methanol solution of phthalic acid, 23 ml of the 10% by weight aqueous solution of 4-methylphthalic acid, 28 ml

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of sulfuric acid having a concentration of 0.5 mol/liter, 5 ml of the 5% by weight aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 0.5 g of phenoxy ethanol, and 0.1 g of benzoisothiazolinone, and then water was added to the mixture to make the total amount 750 g to prepare a coating solution, and directly before coating, the coating solution was mixed with 26 ml of 4% by weight chrome alum by a static mixer and sent to a coating die such that the coating amount became 18.6 ml/m<sup>2</sup>.

The viscosity of the coating solution measured by a B-type viscometer was 17 (mPa s) at 40°C (No. 1 rotor, 60 rpm).

(Preparation of coating solution of 2nd protective layer of emulsion layer surface)

In water was dissolved 80 g of inert gelatin, to the gelatin solution were added 102 g of the 27.5% by weight solution of the methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization weight ratio 64/9/20/5/2) latex, 3.2 ml of the 5% by weight solution of an N-perfluorooctylsulfonyl-N-propylalanine potassium salt, 32 ml of the 2% by weight aqueous solution of polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether (ethylene oxide average polymerization degree = 15), 23 ml of the 5% by weight solution of Aerosol OT (manufactured by American Cyanamid Company), 4 g of polymethyl methacrylate fine particles (mean particle size

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0.7  $\mu\text{m}$ ), 21 g of polymethyl methacrylate fine particles (mean particle size 6.4  $\mu\text{m}$ ), 1.6 g of 4-methylphthalic acid, 4.8 g of phthalic acid, 44 ml of sulfuric acid having a concentration of 0.5 mol/liter, and 10 ml of benzoisothiazolinone, and water added to the mixture to make the total weight 650 g. Then, directly before coating, the diluted mixture was mixed with 445 ml of an aqueous solution containing 4% by weight chrome alum and 0.67% by weight phthalic acid by a static mixer to provide a coating solution of the surface protective layer and the coating solution was sent to a coating die such that the coating amount became 8.3 ml/m<sup>2</sup>.

The viscosity of the coating solution measured by a B-type viscometer was 9 (mPa s) at 40°C (No. 1 rotor, 60 rpm).

(Preparation of photothermographic material-1)

The back surface of the above-described subbed support were simultaneously double coated with the coating solution of an antihalation layer such that the solid component coated amount of the solid fine particle dye became 0.04 g/m<sup>2</sup> and the coating solution of the back surface protective layer such that the gelatin coated amount became 1.7 g/m<sup>2</sup>, followed by drying to form the back layers.

The opposite subbed surface of the support to the back surface were simultaneously multilayer-coated by a slide bead coating system in the order from the subbed surface, an emulsion layer (coated silver amount of the silver halide 0.14 g/m<sup>2</sup>), an

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interlayer, a 1st protective layer, and a 2nd protective layer to prepare a sample (Sample No. 1) of the photothermographic material. The coating and drying conditions were as follows.

Coating was carried out at a speed of 160 meters/minute, the gap between the coating die head and the support was from 0.10 to 0.30 mm and the pressure of the reduced-pressure chamber was lowered by 196 to 882 Pa than the atmospheric pressure. The support was static-eliminated by an ionized blast before coating.

After cooling the coated solutions by a blast of a dry-bulb temperature of 10 to 20°C in the successive chilling zone, the coated support was conveyed by a non-contact type conveyer and dried by a helical non-contact type dryer with a drying blast of a dry-bulb temperature of from 23 to 45°C and a wet-bulb temperature of from 15 to 21°C.

After drying, the coated layers were subjected to moisture conditioning at 25°C and a relative humidity of from 40 to 60%, and thereafter, the coated support was heated such that the film surface temperature became from 70 to 90°C. After heating, the coated support was cooled until the film surface became 25°C.

The matted degree of the photothermographic material prepared was 550 seconds at the light-sensitive layer side and 130 seconds at the back surface as the Beck smoothness. Also, the pH of the film surface of the light-sensitive layer surface side was 6.0.

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(Preparation of photothermographic material-2)

By following the same procedure as the case of the photothermographic material-1 (Sample No. 1) except that the coating solution of the emulsion layer was changed as described below and the yellow dye compound 15 of the antihalation layer was removed, a photothermographic material-2 (Sample No. 2) was prepared.

(Preparation of coating solution of emulsion layer (light-sensitive layer))

A mixture of 1.1 g of the 20% by weight dispersion of the pigment obtained as described above, 103 g of the fatty acid silver salt dispersion, 5 g of the 20% by weight aqueous solution of polyvinyl alcohol PVA-205 (manufactured by KURARAY CO., LTD.), 26 g of the 25% by weight dispersion of the reducing agent complex described above, 8.2 g of the total amounts of 1 : 3 (weight ratio) of the organic polyhalogen compound dispersions-3 and -4, 6.2 g of 10% dispersion of the mercapto compound, 106 g of the SBR latex (the latex of -St(70)-Bu(27)-AA(3)-, Tg: 23°C) subjected to the ultrafiltration (UF) purification and pH control, and 18 ml of the 5% by weight solution of the phthalazine compound was mixed well with 10 g of the silver halide mixed emulsion A directly before coating to prepare a coating solution of emulsion layer, and the coating solution was sent to a coating die as it was such that the coating amount became 70 ml/m<sup>2</sup>, and coated.

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By following the same procedures as the cases of the sample Nos. 1 and 2 of the photothermographic material except that the same amount of each of the fluorine-based surface active agents shown in Table 1 below was used in place of the N-perfluorooctylsulfonyl-N-propylalanine potassium salt and polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether (ethylene oxide average polymerization degree = 15) in the protective layer for back surface and the 2nd protective layer of emulsion layer surface, light-sensitive materials 001 to 010 and 011 to 020 were prepared.

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Table 1'

Sample No.	Base Formula	Fluorine-based Surface Active Agent	White Spots	Note
1	1	Comp. A	8	Comparison
2	2	Comp. A	7	Comparison
001	1	FC-1	10	Comparison
002	1	FC-2	9	Comparison
003	1	FC-3	11	Comparison
004	1	FS-18	3	Invention
005	1	FS-19	3	Invention
006	1	FS-21	2	Invention
007	1	FS-26	4	Invention
008	1	FS-38	3	Invention
009	1	FS-39	3	Invention
010	1	FS-41	2	Invention
011	2	FC-1	9	Comparison
012	2	FC-2	8	Comparison
013	2	FC-3	10	Comparison
014	2	FS-18	2	Invention
015	2	FS-19	1	Invention
016	2	FS-20	1	Invention
017	2	FS-22	2	Invention
018	2	FS-27	3	Invention
019	2	FS-38	2	Invention
020	2	FS-40	1	Invention
	1	FC-4	10	Comparison
	1	FS-13	3	Invention
	2	FC-4	9	Comparison
	2	FS-13	2	Invention

Comp. A = N-perfluorooctylsulfonyl-N-propylalanine  
potassium salt and polyethylene glycol mono(N-  
perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether

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The structure of the surface active agents FC-1, FC-2 and FC-3 can be found on page 80 of the specification. The structure of the surface active agents FS-18, FS-19, FS-21, FS-26, FS-38, FS-39 and FS-41 can be found on pages 11-12 of the specification. The structure of the surface active agents FC-4 and FS-13 are described above.

#### Conclusions

The data in Table 1' shows that photothermographic materials incorporating surface active agents having an alkylene group bonded directly to the fluorinated end group have far superior resistance to white spots than photothermographic materials incorporating surface active agents which do not have an alkylene group bonded directly to the fluorinated end group. For instance, there is at least a 175% increase in white spots in the photothermographic material of Comparative Sample No. 2 having 7 white spots whereas Inventive Sample No. 007 has 4 white spots. The improvement is even more dramatic when the inventive surface active agents are compared to the surface active agent disclosed by Toya (herein labeled "FC-4").

Based on the above-described data, the improved properties of the inventive photothermographic material incorporating



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surface active agents having an alkylene group bonded directly to the fluorinated end group are unexpected based on the disclosure of Toya, either taken alone or in combination with the prior art.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 9 day of January, 2003

By: Yasuhiro Yoshioka

Mr. Yasuhiro Yoshioka